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LIGHT-OFF TEMPERATURE DETERMINATION OF OXIDATION CATALYST USING FOURIER TRANSFORM INFRARED TECHNIQUE

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Light-off temperatures of oxidation catalysts are considered as one of the important parameters for catalyst performance evaluation. In this study, the in situ Fourier Transform IR technique was developed and used to determine the light-off temperatures and reaction products of three three-way automotive catalysts with 20 torr monomethylamine in air at 0.5 L/min flow rate. Light-off temperatures were 140, 143, and 170 °C for Davison, Allied-Signal, and Degussa oxidation catalysts, respectively. CO, CO_2, H_2O, and nitric acid were the major oxidation products. The activation energies of formation of CO and CO_2 on the catalysts were also determined.

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PREFACE

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LIGHT-OFF TEMPERATURE DETERMINATION OF OXIDATION CATALYST USING FOURIER TRANSFORM INFARED TECHNIQUE

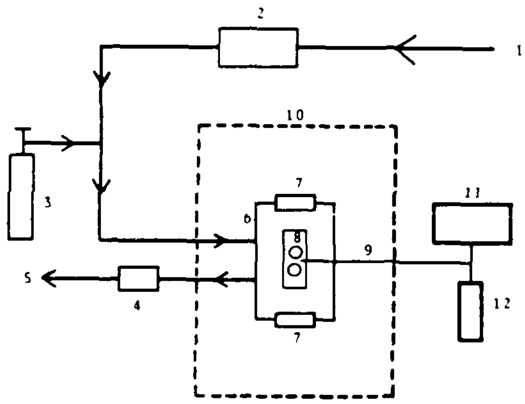
1. INTRODUCTION

There are various techniques to evaluate the performance of oxidation catalysts. Measurements of surface composition, surface structure, surface area, porosity, acidity, and dispersion of active metals of oxidation catalysts, etc., can be related to the catalyst performance.[1] Other methods such as the decoloration of the indigo carmine solution to correlate the catalytic activity with the flash point[2] and the recorder-equipped calorimeter technique to determine the ignition time, maximum temperature, and maximum combustion temperature[3] were used. For an oxidation catalyst, however, one direct measurement of its performance is to determine its light-off temperature, the temperature at which significant oxidation reactions occur. In general, it is true that the lower the light-off temperature, the more effective will be the catalyst performance.[4-5] Indeed, this correlation was used in the past to select the optimum reduction temperature and the duration of reduction for the preparation of the best Ni-containing catalyst.[6] We developed an in situ Fourier Transform IR (FTIR) technique for simultaneously determining the light-off temperatures and identifying catalytic oxidation products of oxidation catalysts. Using this newly developed technique, three three-way automotive catalysts were evaluated. The details of the subject technique and the results of catalyst performance evaluation are described below.

2. EXPERIMENTAL PROCEDURES

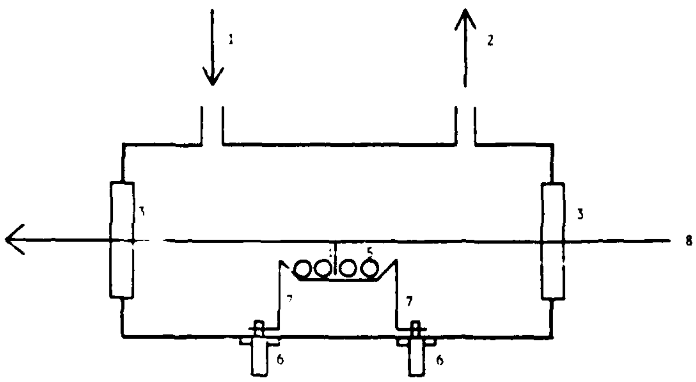
Anhydrous monomethylamine (MMA) used in this study was supplied by Matheson Gas Products with a purity of 99.99%. MMA was used as received without further purification. Three three-way automotive oxidation catalysts were provided by Allied-Signal (UOP# 4576-136), Davison (alumina catalysts code 701), and Degussa (TWC-1, MS-599). Bead-type catalyst samples were dried overnight in an oven at 110 °C before use.

The schematic diagram of the in situ FTIR catalyst light-off temperature measurement system is shown in Figure 1. The measurement system consists of a flow IR cell, a K-type thermocouple with a chart recorder and digital thermometer display, a mass flow controller, a lecture bottle of MMA, a MKS pressure gauge, and Nicolet FTIR Model 60SX. The details of the flow IR cell are illustrated in Figure 2. This flow IR cell has 10 cm optical pathlength and a 25 x 4 mm NaCl window, the heating element and sample holder, the gas inlet and outlet, and the thermocouple. The thermocouple is positioned in the proximity of the sample to measure the temperature of an oxidation reaction. For accurate determination of the light-off temperature of a catalyst, a chart recorder was used along with a digital thermometer display.



1. Compressed Air
2. Mass Flow Controller
3. Gas Lecture Bottle
4. MKS Pressure Gauge
5. Exhaust
6. IR Cell
7. IR Window
8. Catalyst Sample
9. Thermocouple
10. Sample Compartment of Nicolet FTIR Model 60SX
11. Chart Recorder
12. Digital Thermometer Display

Figure 1. FTIR Catalyst Light-Off Temperature Measurement System



1. Gas Inlet
2. Gas Outlet
3. IR Window
4. Thermocouple
5. Catalyst Sample
6. Electrical Leads for Heating
7. Heating Element and Sample Holder
8. IR Beam

Figure 2. Schematic Diagram of the Flow IR Cell

Initially, a correlation between the temperature setting on the heater controller and the temperature reading on the digital thermocouple display was obtained. The temperature reading was about 30 to 40% of the temperature setting on the heater controller. To run an experiment, the IR background spectra were taken at various temperatures with the flow IR cell purged with dried air at 0.5 L/min flow rate, which was automatically controlled by a Matheson mass flow controller. Background spectra were taken in the mixture of dried air and 20 torr MMA in the absence of catalyst. The background spectra essentially remain the same in the temperature range of 25-363 °C indicative of no catalytic activity due to the heating element. For catalyst evaluation, three catalyst beads were placed on the sample holder (the heating element with a V-shape), and the thermocouple was positioned in the proximity of catalyst beads. After the light-off temperature measurement system was assembled, the flow IR cell was evacuated with a vacuum pump, and MMA was injected and maintained at 20 torr. The system was disconnected with the vacuum pump, and the IR cell was brought to ambient pressure with compressed air at 0.5 L/min flow rate. The heater controller was set at around 200 °C (equivalent to the thermocouple reading of 80 °C), and the setting was increased 10° every 15-20 min. During this time, an IR spectrum was taken between 4,000 and 400 cm^{-1} with 4 cm^{-1} resolution. Normally, 32 scans were taken for each IR spectrum at every temperature setting. Significant oxidation reaction was detected around 140 °C thermocouple reading on the digital thermometer display. The determination of light-off temperature was carried out using the chart of the temperature recorder. The light-off temperatures were reproducible with repeated on and off cycles of MMA. These procedures were used for three three-way automotive oxidation catalysts provided by Davison, Allied-Signal, and Degussa.

3. RESULTS AND DISCUSSION

Typical IR spectra at various temperatures are illustrated in Figures 3-5 with Davison three-way catalyst samples. At 94 °C, the IR features are very much the same as MMA as shown in Figure 3. When the temperature was increased to 190 °C (as shown in Figure 4), peaks around 2,154 and 2,351 cm^{-1} respectively corresponding to CO and CO_2, and peaks around 1,540 and 3,770 cm^{-1} corresponding to H_2O grow substantially. As the temperature reaches 261 °C, the formation of HNO_3 and the effect of water on nitric acid[7-9] corresponding to the bands centered around 2,964, 1,700, 1,320, 760 cm^{-1} appear to be the major reaction products, Figure 5. For each sample, at least three experiments were conducted, and the light-off temperatures were determined using the charts from the temperature recorder. The average light-off temperatures for three three-way automotive catalysts are shown in Table 1. In the increasing light-off temperature, the order is Davison, Allied-Signal, and Degussa catalysts. For Davison and Allied-Signal samples, the light-off temperatures are very close to each other. However, for the Degussa sample, the light-off temperature is about 30 °C higher than that of Davison and Allied-Signal.

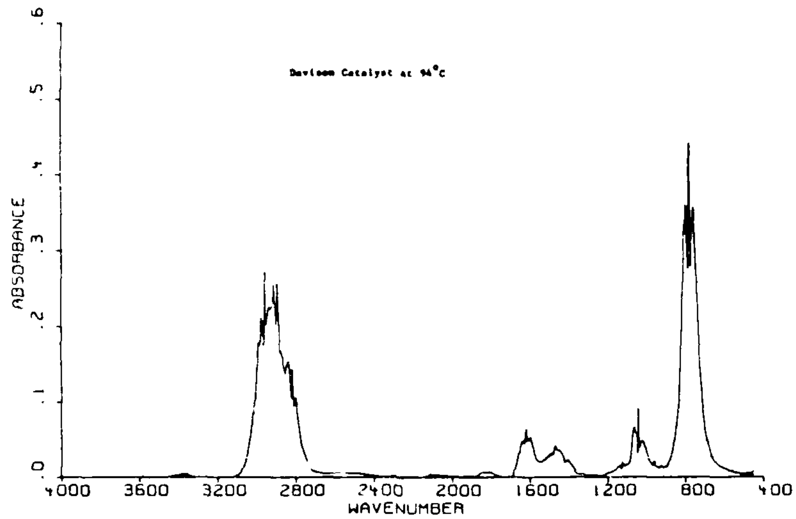


Figure 3. IR Spectrum of MMA with Davison Catalyst at 94 °C

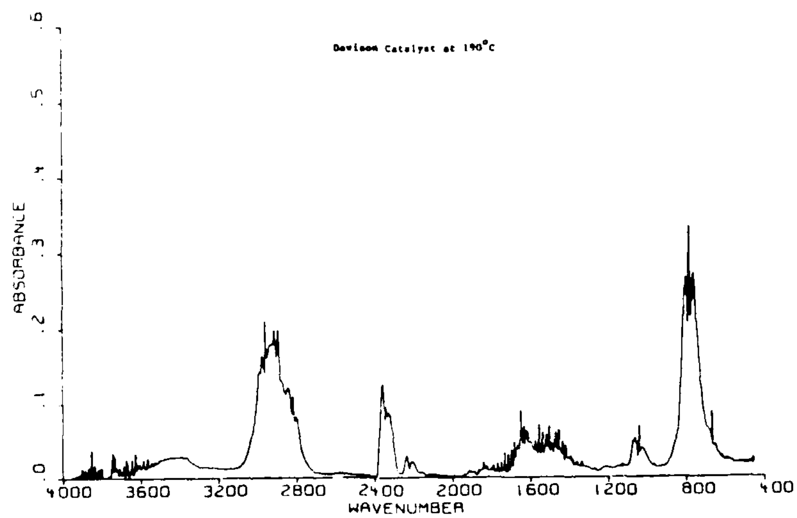


Figure 4. IR Spectrum of MMA with Davison Catalyst at 190 °C

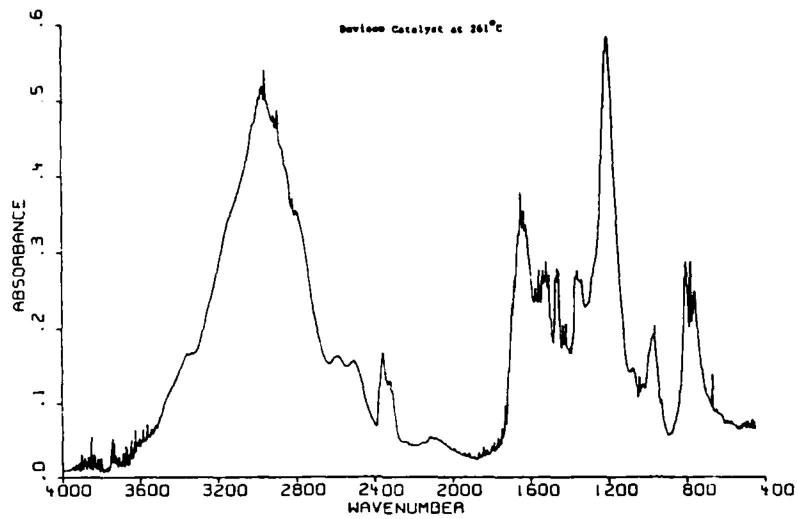


Figure 5. IR Spectrum of MMA with Davison Catalyst at 261 °C

Table 1. Light-Off Temperatures of Three-Way Automotive Catalysts

Davison	140 °C
Allied-Signal	143 °C
Degussa	170 °C

The absorbance of CO and CO_2 were taken from the IR spectra at various temperatures, and Arrhenius plots were obtained as shown in Figures 6-7. The activation energies of formation of CO and CO_2 were found using the relation of slope = $-E_a/R$, where E_a is the activation energy and R is the ideal gas constant, which is equal to 1.987 cal/mol/K. Table 2 shows the activation energies of formation of CO and CO_2 for three three-way automotive catalysts. In general, the activation energy of formation of CO_2 is lower than that of CO, which is consistent with the free energy of formation of CO_2 which is lower than that of CO. Note that the lower the light-off temperature, the lower the activation energy of formation for both CO and CO_2 from the three-way automotive catalysts investigated.

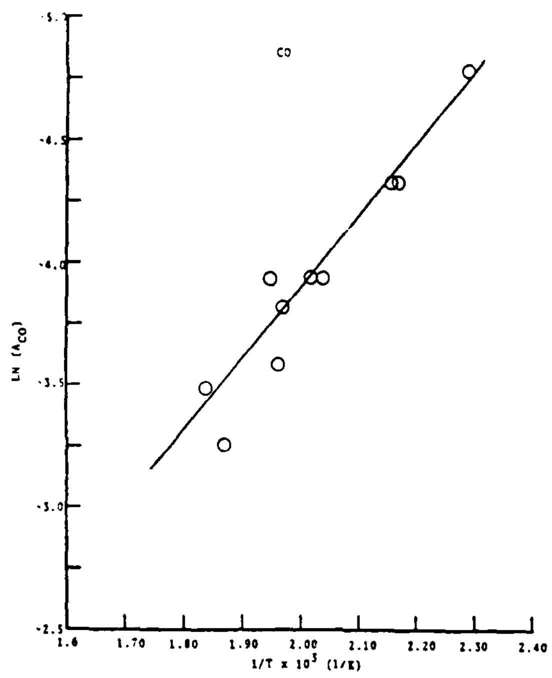


Figure 6. Arrhenius Plot of CO on Davison Oxidation Catalyst

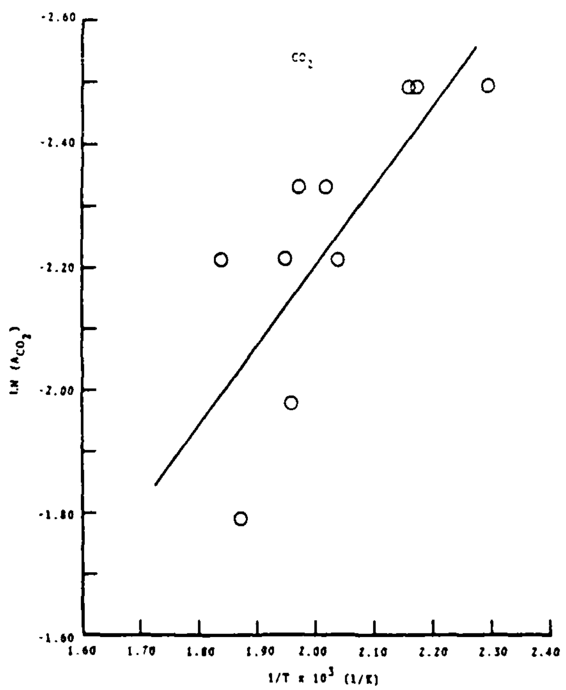


Figure 7. Arrhenius Plot of CO_2 on Davison Oxidation Catalyst

Table 2. Activation Energy of Formation, Kcal/mol

	CO_2	CO
Davison	2.29	6.41
Allied-Signal	2.68	12.07
Degussa	5.76	21.60

4. SUMMARY

The results are summarized as follows:

- An in situ FTIR technique was developed and demonstrated for the light-off temperature determination and the identification of reaction products of oxidation catalysts.

- Light-off temperatures with 20 torr MMA for Davison, Allied-Signal, and Degussa three-way automotive catalysts were 140, 143, and 170 °C in air with 0.5 L/min flow rate, respectively.

- The reaction products were CO, CO_2, H_2O, and HNO_3 for three three-way automotive catalysts.

- The activation energies of formation for CO and CO_2 on three three-way catalysts were determined. For CO, they are 6.41, 12.07, and 21.60 Kcal/mol; and for CO_2, they are 2.29, 2.68, and 5.76 Kcal/mol, for Davison, Allied-Signal, and Degussa three-way automotive catalysts, respectively.

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